Reaction between Polyol-Esters and Phosphate Esters in the Presence of Metal Carbides

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Abstract

The reaction of metal carbides with polyol esters found in aerospace lubricants and phosphate esters commonly used as additives was investigated. Carbides were of particular interest since modern materials under consideration at high temperature bearings have surfaces that are primarily metal carbides. Vanadium and chromium carbide were found to react with the ester and phosphate ester by a transesterification reaction, producing an alkyl phosphate which is less stable than the aromatic phosphate esters. In the process, the metal carbide is converted to the metal phosphate and metal polyphosphate, evidenced by the infrared and Raman spectra of the solid residue and presence of a large amount of phosphorus found on the surface of the material. Arguments for the mechanism of this reaction are based on the examination of the reaction vanadium carbide and chromium carbide with an extensive series of model compounds, prepared for this study. The model compounds allow several intermediates to be identified and the reaction pathway to be determined.

Keywords

 Synthetic Lubricant, Additives, Metal Carbides

Introduction

In the desire to increase the efficiency and performance of jet turbine engines, a number of bearing materials that can withstand higher temperatures and stresses have been developed and tested (Trivedi, 2011). The composition of several of the modern alloys is shown in Table 1. These materials typically have enhanced hardness due to the formation of a thin coating on the surface of the material (Ragan, 2002). These coatings are frequently formed during the heat treating process through the introduction of a carbon source such as methane or carbon monoxide (Brusilovskii,, 2001). Chemical reaction at the surface results in a thin coating that is

much harder than the bulk material. Upon further heat treating, the structure of the carbides changes and additional carbides form on the surface (Pippel, 1999). The coating is thought to contain regions consisting of diamond like carbon, and other regions that contain metal carbides between the grain boundaries of the material (Meng, 1993).

TABLE 1 COMPOSITION OF CURRENT STEEL BEARINGS(ROSADO)

Steel	%C	%V	%Cr	%Mo
M-50	0.8-0.85	4-4.25	0.9-1.0	4-4.5
M-50NiL	0.11-0.15	4-4.25	1.1-1.3	4-4.5
52100	0.98-1.1	1.3-1.6		
Pyrowear 675	0.07	13	0.6	1.8
CSS42	0.12	14	0.6	4.75
Conudor 30	0.31	15.2		

The increase in the hardness of these new bearing materials has been attributed to having the correct balance between carbon and the alloying elements, particularly chromium, molybdenum, tungsten, vanadium and cobalt which are known to form stable carbides during the heat treating process (Saba 2012). Previous studies of a carburized stainless steel has shown a surface that consists of about 40% by volume chromium/iron carbide $(Cr,Fe)_7C_3$ on top of a layer of a more metal rich carbide phase of $(Cr,Fe)_{23}C_6$ (Tabet, 2003). Other studies have shown that carbides of molybdenum, tungsten and presumably chromium form preferentially to the iron carbide (Fe_3C), providing a surface that contains little iron (Shtanski, 1997).

Aviation lubricants typically consist of a polyol ester base stock, which is supplemented with amine antioxidants (PANA and DODPA) and phosphate ester anti-wear additives (Gschwender, 2000). The

phosphate esters are known to react with traditional bearing surfaces to form a bonded metal polyphosphate which lubricates the surfaces. These reactions require the presence of iron oxide at the surface to react with the phosphate ester. Changes in the surface chemistry or surface composition can have a dramatic effect on the rates and mechanism of these reactions. Previous work has shown that phosphate esters are not effective if iron oxide is absent. Studies by Gellman et.al. have shown that ceramics must be treated with Fe(CO)$_5$ in order for phosphates to be reactive (Ren, 2001). Our previous work has shown that metal carbides, while failing to be reactive towards ester based lubricants and phosphate esters individually, become very reactive when both phosphate esters and polyol esters are present (Chen, 1995). In this report, the reactions between phosphate esters, polyol esters and metal carbides are reported. These studies provide a basis for the selection of lubricants and additive packages for use with advanced bearing materials.

Experimental Methods

Sample Preparation

1) Lubricant Model Compounds

Lubricant model compounds have been prepared using methods that have been previously described (Zhang, 2011; Padmaja, 2012). The model compounds were characterized with viscosity, infrared spectroscopy and NMR spectro-scopy giving results that are consistent with the literature (Niedzielski,1976; Smith, 1992). Infrared spectra showed no peak in the 3200-3600 cm^{-1} region, indicating that there is no residual acid or unreacted polyol in the sample. Formulated esters were prepared by dissolving a weighed quantity of tricresyl phosphate in a weighed quantity of the synthetic ester.

2) Metal Carbides

Metal carbide powders purchased from Alfa/Aesar and used as received. Single crystal vanadium carbide (111 face) was purchased from Applied Physics Laboratories as a 2.0 mm crystal. The sample was used as received.

Testing Methods

1) Sealed Tube Tests

Sealed tube tests at 350℃ for four hours were conducted using methods that have been previously described (Saba, 2002).

2) Flowing Gas Tests

Flowing gas decomposition reactions were studied using the apparatus that contained a reaction tube, that was fitted with a bubbler connected to a glass trap. The reaction tube was heated in an oil bath at 200℃ with a gas flow rate of 50 ml/min. for a period of 4 hours. A 10.0 mL sample of the ester or ester with phosphate ester was added to 0.100 g of the metal carbide. A flow of either nitrogen or air was started and the reaction tube was immersed in an oil bath. The trap was cooled to -78℃ in order to trap any of the volatile products.

Physical Methods

1) Infrared Spectroscopy

Infrared spectra of the model compounds were obtained in transmission mode on a Perkin-Elmer infrared spectrometer. Infrared spectra of the solid carbides were measured using an ir-plan microscope, in reflectance mode using a germanium ATR crystal. In the case of the solid samples, they were placed on a small mirrored surface. Several areas of the sample were examined in order to ensure that the results were representative of the entire sample.

2) Raman Spectroscopy

Raman spectra were collected using a Delta-Nu Raman system with a diode laser (785nm) for excitation. Data was collected from 200-3400 cm^{-1}. An acquisition time of 2 seconds with 100 spectra averaged was used to obtain a spectrum with adequate signal to noise ratio. Samples were placed in melting point capillaries and the beam was focused for maximum intensity for each sample.

3) Scanning Electron Microscopy

SEM pictures were obtained using a Jeol model 6460LV scanning electron microscope with EDAX attachment for elemental analysis. Samples were attached to an aluminum block with carbon tape.

4) Gas Chromatography/Mass spectrometry

The volatile components of the reaction mixture were analyzed by gas chromatography/mass spectrometry using methods previously described (Johnson, 2002).

Results and Discussion

Sealed tube reactions with each of the synthetic esters, TCP and a metal carbide at 325℃ for a period of 4 hours all showed significant reaction. Similar reaction where any one of the components was absent showed little or no reaction.   The results, given as the percentage of ester remaining for a series with vanadium carbide are shown in Table 2 and with chromium carbide are shown in Table 3.

A comparison of the relative reactivities of the metal carbides indicates that vanadium carbide is substantially more reactive than chromium carbide and the reactivity of the esters increases as the length of the carboxylic acid decreases. Similarly, it is

TABLE 2. REACTIVITY OF PREPARED ESTERS WITH VANADIUM CARBIDE WITH AND WITHOUT THE PRESENCE OF TRI-CRESYL PHOSPHATE SHOWN AS THE PERCENT LUBRICANT REMAINING AFTER REACTION AT 350℃ FOR 4 HOURS IN A SEALED TUBE

Polyol	Acid Chain Length					
	C-5	C-6	C-7	C-8	C-9	C-10
Ester without Tricresyl Phosphate						
NPG	30	40	40	60	80	80
TMP	75	>90	>90	>90	>90	>90
PE	>90	>90	>90	>90	>90	>90
Ester with Tricresyl Phosphate						
NPG	<5	<5	<5	<5	<5	<5
TMP	5	10	10	15	25	40
PE	45	60	70	85	>90	>90

TABLE 3. REACTIVITY OF PREPARED ESTERS WITH CHROMIUM CARBIDE WITH AND WITHOUT THE PRESENCE OF TRI-CRESYL PHOSPHATE SHOWN AS THE PERCENT LUBRICANT REMAINING AFTER REACTION AT 350℃ FOR 4 HOURS IN A SEALED TUBE

Polyol	Acid Chain Length					
	C-5	C-6	C-7	C-8	C-9	C-10
Ester without Tricresyl Phosphate						
NPG	80	85	90	>90	>90	>90
TMP	90	>90	>90	>90	>90	>90
PE	>90	>90	>90	>90	>90	>90
Ester with Tricresyl Phosphate						
NPG	<5	<5	<5	<5	<5	<5
TMP	25	35	35	40	40	50
PE	65	80	85	>90	>90	>90

observed that the neopentyl glycol (NPG) esters are more reactive than the trimethanolopropane (TMP)

esters which in turn are more reactive than the pentaerythritol (PE) esters (Eychenne, 1998). The results demonstrate that the three components must all be present in the sealed tube for any reactivity to be observed.

Analysis of the Volatile Products

In an effort to elucidate the reaction mechanism and develop a clearer understanding of the reactivity of metal carbides, the reactions were studied under lower temperature conditions with a flow of gas where the initial products of the decomposition could be trapped. These reactions failed to be completed, however several reaction products were observed. Of particular interest was the trap samples, which would be expected to contain little of the unreacted lubricant, but significant quantities of the initial products formed in the reaction. The GC/MS total ion chromatogram for the trap sample in the reaction of a single component ester with TCP and vanadium carbide is shown in Figure 1.
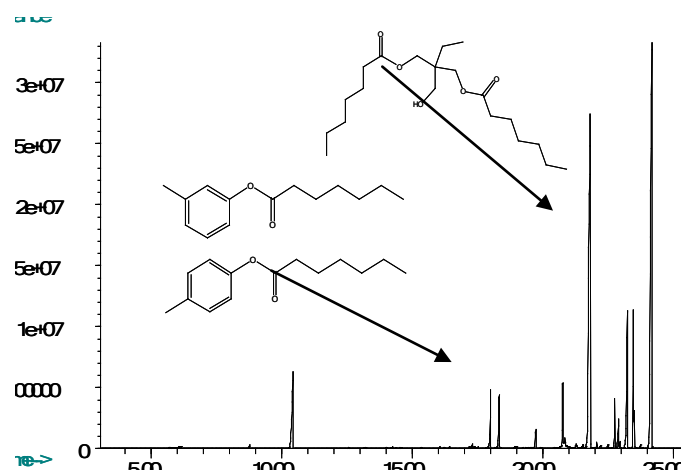

FIG. 1. TOTAL ION CHROMATOGRAM FOR THE TRAP SAMPLE IN THE REACTION OF VANADIUM CARBIDE WITH TCP AND TMP-C7 AT 200℃ IN AIR.

The products of the reaction are indicative of an early step being the trans-esterification reaction of the phosphate ester with the lubricant ester. The peaks due to these products have been identified in Figure 1 and appeared at 17.9 and 18.2 minutes retention time. Other peaks have been identified as a product that contains the phosphate ester from the poly-alcohol of the lubricant ester. These observations are consistent with an initial step which partially decomposed the phosphate ester to give an alkyl phosphate ester. These alkyl esters are more reactive, proceeding to deposit phosphate onto the surface of the substrate

(Sung, 2002). There is also evidence for the generation of gases in several of these reactions, which lead to the destruction of the sealed tube. Minor products are observed, including an ester that also contains a carbon-carbon double bond. These products illustrating the complexity of these reactions, may also serve as a source of hydrogen for the formation of methane from the carbide ion displaced by the phosphate ion.

Reactivity of the Solid Metal Carbides

The metal carbide samples were examined before and after reaction by scanning electron microscopy, infrared microscopy and Raman spectroscopy. The results of these experiments show that the surface of the carbide does participate in the reaction when all three components are present. Examination of the unreacted powders using scanning electron microscopy indicates a rough surface. The scanning electron micrographs of unreacted chromium carbide and vanadium carbide are shown in Figure 2. Below each of the pictures is the EDAX spectrum.   The pictures indicate a small particle size, each of which is observed to have sharp edges, consistent with a microcrystalline powder. The elemental analysis shows only the expected metal and carbon. The analysis of carbon in the powder is not reported due to the possibility of the carbon signal being increased by the carbon tape used to attach the sample to the aluminum block. There are no signals observed for phosphorus or any other element. A sample of single crystal vanadium carbide was also obtained and the 1,1,1 face was allowed to   react with lubricant and phosphate ester. Due to the low surface area of the material, no evidence of reaction (visual or change in composition of oil) was observed under the conditions previously used.

Examining the samples after reaction with the ester based lubricant and TCP shows a significantly different structure and composition. The rough edges present before reaction have been smoothed and rounded, as visual evidence of chemical change. The vanadium carbide sample after reaction has (figure 3) substantially different elemental composition. The changes in elemental composition of the surface are consistent with the formation of vanadium phosphate. Oxygen analysis by EDAX is not very reliable, but the
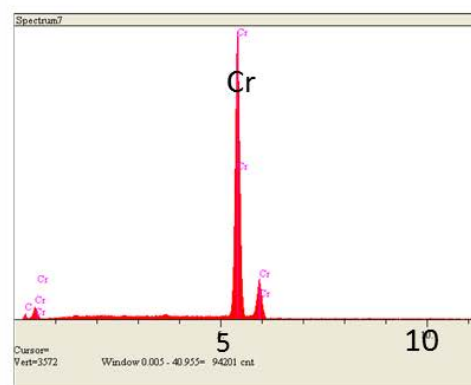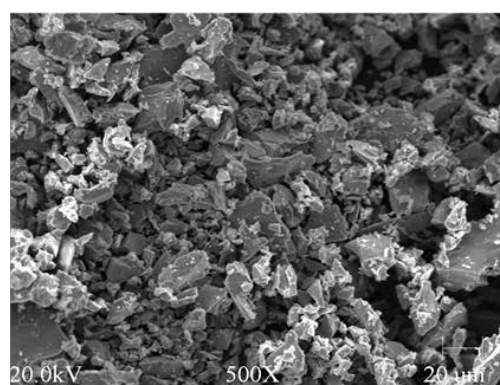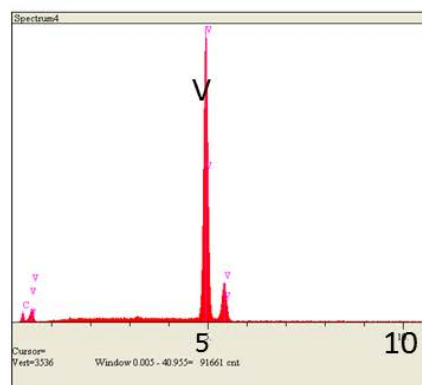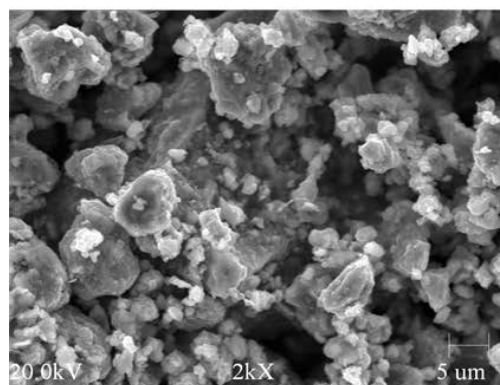

FIG。 2 SCANNING ELECTRON MICROGRAPHS OF UNREACTED VANADIUM CARBIDE (TOP) AND CHROMIUM CARBIDE (BOTTOM) SHOWING THE ELEMENTAL COMPOSITION OF THE SURFACE AS MEASURED USING X-RAY FLUORESCENCE.
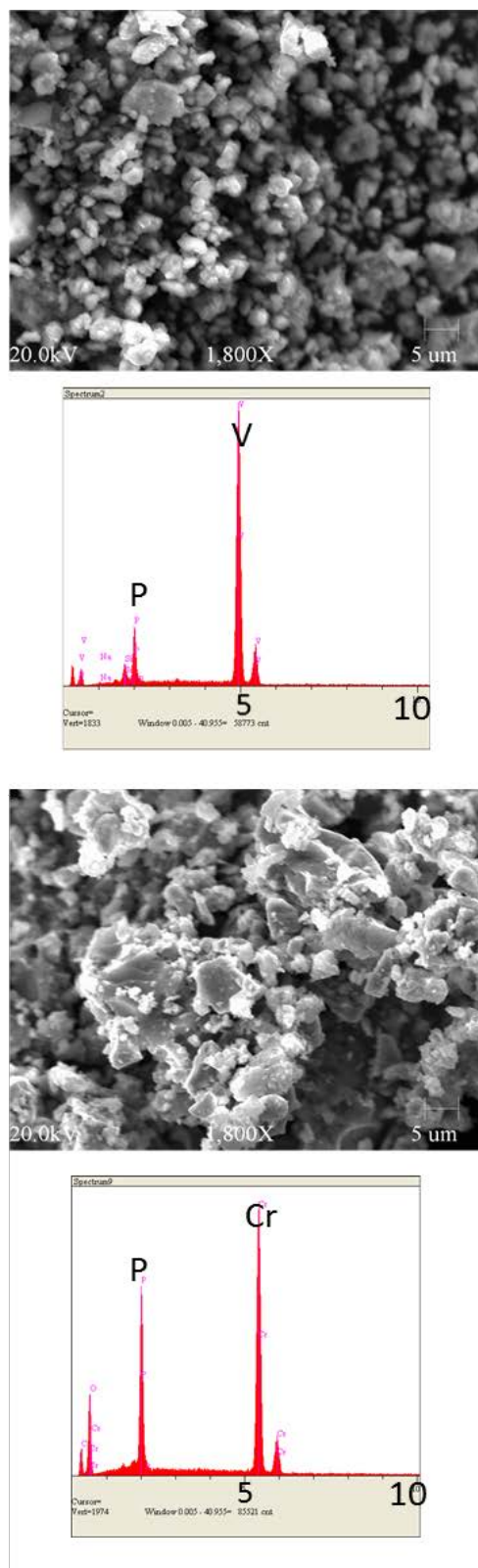
FIG. 3 SCANNING ELECTRON MICROGRAPHS OF VANADIUM CARBIDE (LEFT) AND CHROMIUM CARBIDE (RIGHT) AFTER REACTION WITH TCP AND LUBRICANT ESTER SHOWING THE ELEMENTAL COMPOSITION OF THE SURFACE AS MEASURED USING X-RAY FLUORESCENCE.

presence of oxygen, along with vanadium and phosphorus is clear in the spectrum. The chromium carbide sample shows similar but less extensive changes in composition than the vanadium carbide sample. The presence of phosphorus and oxygen is indicated by EDAX, however the level is lower than that in the vanadium carbide sample.

The vanadium carbide powder and the surface of the single crystal have been investigated further to determine if the phosphorus was evenly distributed. An elemental map of the surface of the vanadium carbide powder is shown in Figure 4, which shows that while phosphorus is distributed over a large portion of the surface, but not evenly distributed. This may be due to the way in which sealed tube tests are conducted, the solid settles to the bottom of the tube, and only the surface of the solid is exposed to the lubricant and phosphate ester. The phosphorous is distributed evenly over the surface of the single crystal vanadium carbide sample. On a similar note, the percent of phosphorus on the chromium carbide samples varies substantially between regions of the same sample.

The phosphorus map in particular indicates that some of the features observed in the SEM picture are higher in phosphorus content than that in the bulk of the sample. The spherical particle near the center of the sample was chosen for more detailed investigation of its composition. The elemental map of this particle is shown in Figure 5. There is a significant increase in the phosphous content of this sample with a similar decrease in the vanadium content of the sample, as compared with the bulk of the sample. The shape of the particle is also interesting, considering that it is a smooth sphere at the level of magnification in this photo.

A similar group of samples reacted with only TCP showed little change in the surface appearance and only a trace of phosphorus on the surface. These results demonstrate that both the ester based lubricant and the phosphate ester are needed for the reaction.

Raman Spectroscopy

The Raman spectrum of pre and post test samples have been measured in order to determine the structural changes in the surface and to identify the phosphorus containing species incorporated into the
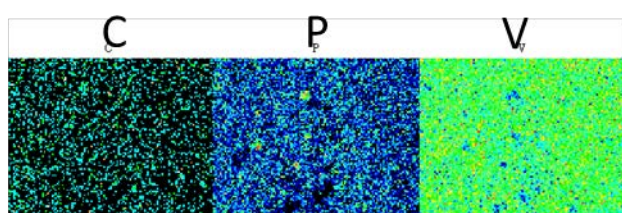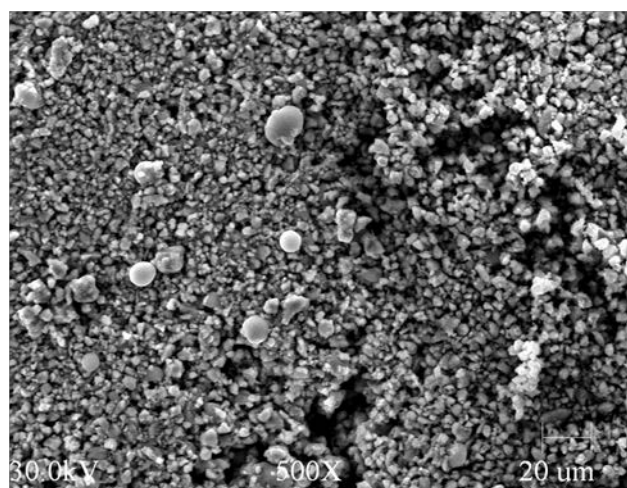
FIG. 4 AN SEM PICTURE AND ELEMENTAL COMPOSITION MAP OF THE SURFACE OF A SAMPLE OF VANADIUM CARBIDE SHOWING THE DISTRIBUTION OF CARBON, PHOSPHORUS AND VANADIUM THROUGH THE SAMPLE.
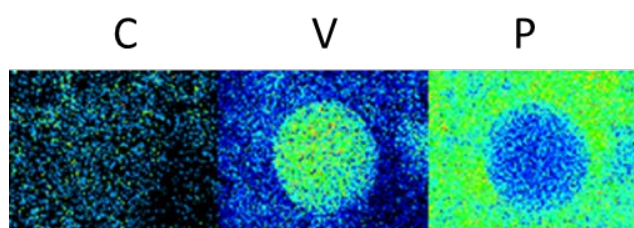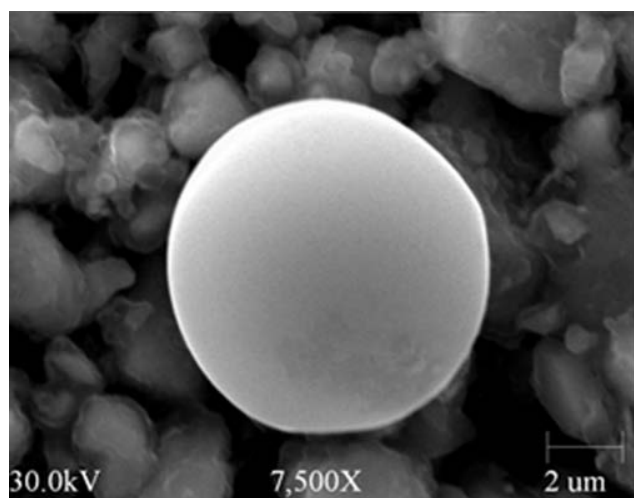

FIG. 5 SEM PICTURE AND ELEMENTAL MAP FOR A PORTION OF A VANADIUM CARBIDE SAMPLE AFTER REACTION WITH LUBRICANT AND PHOSPHATE ESTER.

surface of the solid. The Raman spectra of samples of unused vanadium carbide, vanadium carbide reacted with lubricant ester, phosphate ester and both

lubricant and phosphate esters are shown in Figure 6. The unreacted vanadium carbide and samples reacted with either lubricant ester or phosphate ester show no signals above the baseline noise. The sample reacted with both lubricant and phosphate ester shows two broad features well above the background noise. The primary signals, a broad signal between 825 and 1100 cm^{-1} is indicative of the presence of phosphate. The band is assigned to the asymmetric stretching mode of the phosphate. The high frequency portion of the Raman band is also due to the presence of V=O which is another likely component of the solid. The broad feature indicates that the phosphate is present, not as a single structure, but as a mixture of phosphate, diphosphate and other polyphosphates. The second major feature, a broad peak at about 1650 cm^{-1} is indicative of the formation of polycyclic
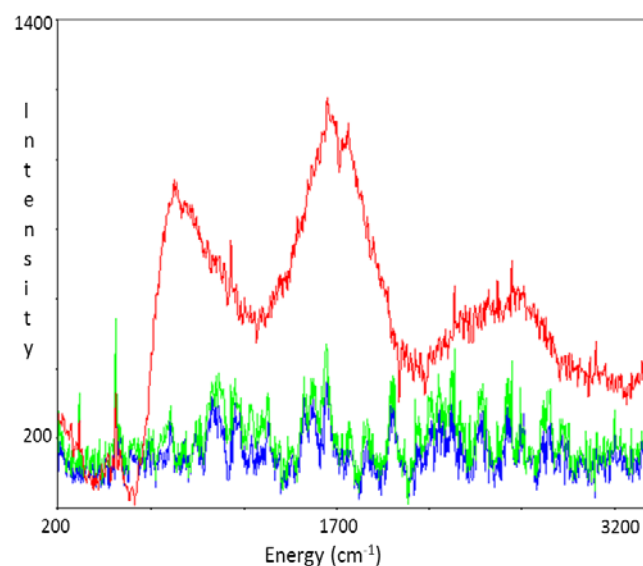

FIG. 6 RAMAN SPECTRA OF VANADIUM CARBIDE SAMPLES AFTER REACTION WITH LUBRICANT ESTER(BLUE), PHOSPHATE ESTER (GREEN) AND BOTH LUBRICANT AND PHOSPHATE ESTERS (RED).

aromatic compounds and possibly amorphous carbon. A comparison of the spectrum of the reacted vanadium carbide sample with the spectra of TCP, lubricant ester and iron(III) phosphate is shown in Figure 7. Previous work on phosphate glasses showed a shift to lower energy for the glass samples as compared with a pure crystalline monophosphate (Bartley, 2001). The shift is attributed to variable environments for the phosphate groups in the glass and the formation of phosphate chains. (Anderson, 1979). The temp-erature dependence of the Raman spectrum of both phosphates and vanadates is another

indication of the changes in structure that these solids undergo upon heating (Kovyazina, 2004).

Examination of the Raman spectra of chromium carbide samples yields a similar series of peaks. The spectra of the chromium carbide samples are shown in Figure 8. The broad peak in the 1500 cm^{-1} region is due to the presence of residual aromatic compounds and the formation of amorphous carbon (Johnson, 2011). Comparison of the spectra of chromium carbide samples with vanadium carbide samples indicates that less of the surface has reacted. This result is in agreement with the observation that chromium carbide is less reactiove than vanadium carbide. Samples of chromium carbide reacted with TCP alone, or lubricant ester show no Raman bands above the noise, indicating little or no reaction.

Infrared Spectroscopy

Infrared spectroscopy, used to further examine the solid residue from these reactions gave similar information as Raman spectroscopy, which are normally considered to be complementary, since infrared is more sensitive to polar or asymmetric vibrations while Raman spectroscopy is sensitive to non-polar or symmetric vibrations (Nakamoto, 2009). The spectrum of unheated vanadium carbide shows the presence of lattice modes due to the metal carbide. The sample after heating shows broad features due to the presence of a mixture of phosphates. This is similar to the features observed in other experiments involving the deposition of phosphates onto metals at high temperatures. Infrared spectra have also been measured for chromium carbide, before and after reaction with ester based lubricant and TCP. Shifts in the vibrational energies of the solids are observed, consistent with the formation of metal polyphosphates at the surface of the metal carbides.

Conclusion

This study has demonstrated that ester based lubricants and phosphate esters have a dramatically enhanced reactivity when exposed to metal carbides. Even under mild conditions of 200 ℃ , including temperatures below engine operating temperatures, reaction has been observed. Reactivity of the esters is increased further by the presence of oxygen. The metal carbides differ significantly in reactivity with
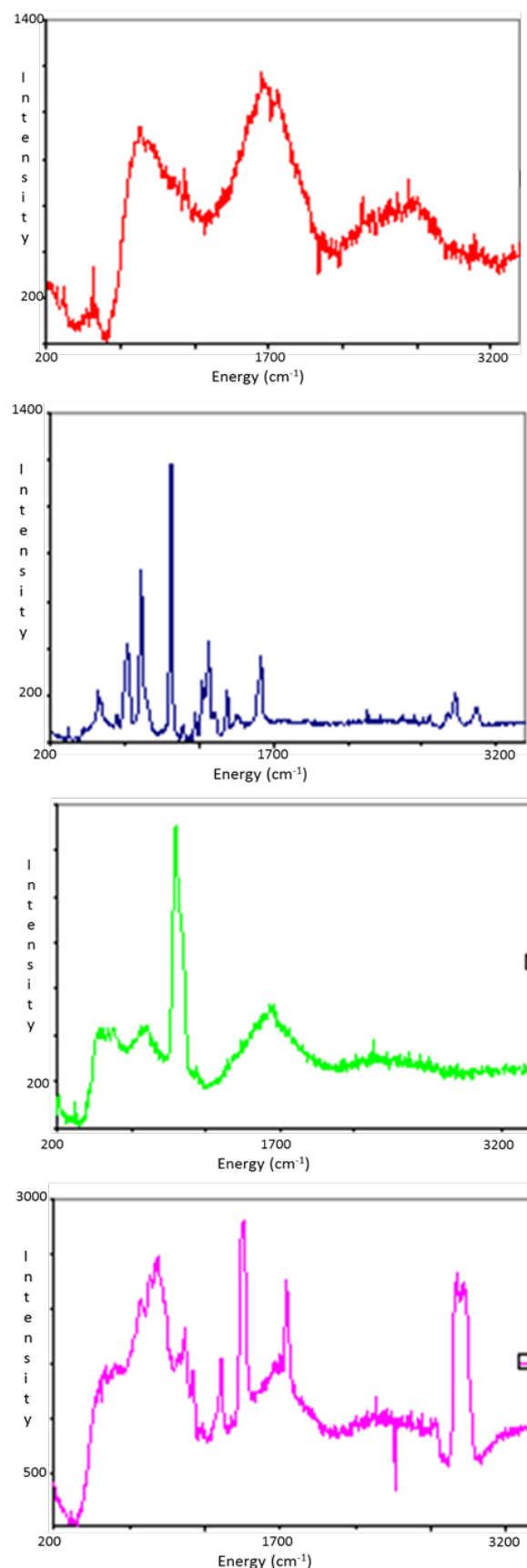

FIG.7 RAMAN SPECTRA OF REACTED VANADIUM CARBIDE(RED), TRI-CRESYL PHOSPHATE(BLUE), IRON (III) PHOSPHATE(GREEN) AND ESTER BASED LUBRICANT(PINK).
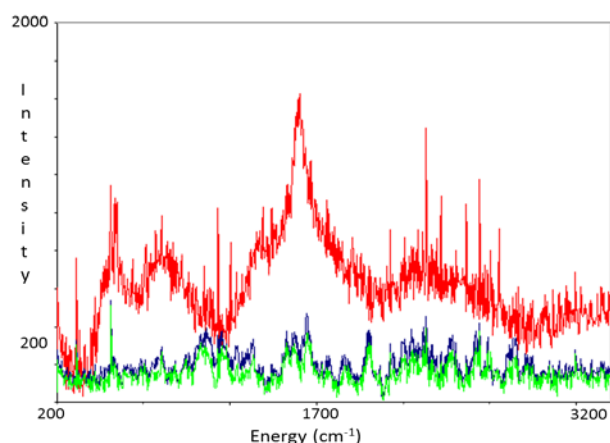
FIG. 8 RAMAN SPECTRA OF CHROMIUM CARBIDE SAMPLES AFTER REACTION WITH LUBRICANT ESTER (BLUE), PHOSPHATE ESTER (GREEN) AND BOTH LUBRICANT AND PHOSPHATE ESTERS (RED).

vanadium carbide more reactive than chromium carbide. The results indicate that care must be taken in changing bearing materials to materials with hard coatings, due to the possible reactions of the coatings.

The organic products of the reaction can be derived from trans-esterification of the phosphate ester and the lubricant ester. One product, aromatic esters appear to be relatively stable compared to phosphate esters of the polyol. These compounds are also of concern due to the neurotoxicity of phosphate esters of TMP. Products formed at the surface also include polyphosphates which are likely to alter the physical properties of the bearing surface.

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